

(19)



(11)

EP 1 878 780 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.01.2008 Bulletin 2008/03

(51) Int Cl.:
C09K 15/08 (2006.01)

(21) Application number: 06014331.0

(22) Date of filing: 11.07.2006

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR
Designated Extension States:
AL BA HR MK YU

(72) Inventors:
• Gijsman, Pieter
6191 NM Beek (NL)
• Jansen, Johan Franz Gradus Antonius
6165 AP Geleen (NL)

(71) Applicant: DSM IP Assets B.V.
6411 TE Heerlen (NL)

(74) Representative: Scheltus, Irma
DSM Intellectual Property
Office Geleen
P.O. Box 9
6160 MA Geleen (NL)

(54) Oxygen-scavenging compositions

(57) The present invention relates to a composition containing an oxidisable carbon-containing component, wherein the composition further contains a vicinal dioxygen containing component. In one embodiment of the invention, the vicinal dioxygen containing component contains at least one 1,2-dioxo-moiety. In another embodiment of the invention, the vicinal dioxygen containing

component contains at least one 1,2-oxo-hydroxy moiety. The present invention further relates to the use of the composition for the preparation of an oxygen-scavenging object like for example a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap.

EP 1 878 780 A1

Description

[0001] The present invention relates to oxygen-scavenging compositions containing an oxidisable carbon-containing component. The present invention also relates to the use of such a composition for the preparation of an oxygen-scavenging object. The present invention further relates to objects containing an oxygen scavenging layer containing such a composition.

[0002] Oxygen-scavenging compositions are well known and are especially useful in the food packaging business. It is known that oxygen can have an effect on the odor and taste of packaged food thereby shortening the shelf life of the food. The oxidisable carbon-containing component present in the oxygen-scavenging compositions react with oxygen thereby reducing or eliminating the odor and/or undesirable taste of food or beverages excessively exposed to oxygen. The incorporation of oxidation catalyst in the oxygen-scavenging compositions accelerates the oxygen-uptake. Typical oxidation catalysts mentioned in the prior art are transition metal catalysts. The most common transition metal catalyst described by the prior art is a cobalt salt. A disadvantage of using transition metal catalysts for accelerating the oxygen uptake is that it will be unavoidable that part of the transition metal will be causing environmental pollution. Needless to say that this is not desirable.

[0003] There is, thus, need for alternative oxidation catalysts with less environmental effects.

[0004] Aim of the invention is a composition containing an oxidisable carbon-containing component wherein the presence of a transition metal catalyst is not necessary.

[0005] This aim is achieved in that the composition further contains a vicinal dioxigen containing component.

[0006] It has surprisingly been found that the vicinal dioxigen containing component is an alternative for a transition metal catalyst. In addition, it has been found that the use of some of said vicinal dioxigen containing components even results in that the oxygen scavenging properties of the composition are more efficient.

[0007] In one embodiment of the invention, the vicinal dioxigen containing component contains at least one 1,2-dioxo-moiety. Preferably, the vicinal dioxigen containing component contains at least one 1,2-dioxo-moiety according to formula I



with X and Y being identical or different from each other, and representing respectively: X, Y: OR, SR, NR₁R₂, R₁, O-M⁺; in which

R, R₁, R₂: a group selected from the groups consisting of H, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₆-C₂₀ aryl group, an optionally substituted C₇-C₂₀ alkylaryl group, and an optionally substituted C₇-C₂₀ arylalkyl group;

M⁺ being a cation

and wherein X and Y may be joint together to form a vicinal dioxo cyclic structure of at least 5 carbon atoms, and/or with any of X or Y representing an oligomeric or polymeric residue, which can optionally be substituted.

[0008] Preferably, X and/or Y being R. More preferably, X and Y being R. Even more preferably, X or Y being an optionally substituted C₆-C₂₀ aryl group or an optionally substituted C₇-C₂₀ arylalkyl group; or X is an optionally substituted C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group. In another preferred embodiment, X is OH or an optionally substituted O-C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group. In still another preferred embodiment of the invention, X and/or Y is an O-M⁺, with M⁺ representing an alkaline metal or earth alkaline metal cation, or an ammonium ion.

[0009] In another embodiment of the invention, the vicinal dioxigen containing component contains at least one 1,2-oxo-hydroxy-moiety. Preferably, the vicinal dioxigen containing component contains at least one 1,2-oxo-hydroxy-moiety according to formula II



with X and Y being identical or different from each other, and representing respectively:

X: OR, SR, NR₁R₂, R, O-M⁺; Y: OR, SR, NR₁R₂, R;

R, R₁, R₂: a group selected from the groups consisting of H, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₆-C₂₀ aryl group, an optionally substituted C₇-C₂₀ alkylaryl group, and an optionally substituted C₇-C₂₀ arylalkyl group,

M⁺ being a cation

and wherein X and Y may be joint together to form a vicinal dioxo cyclic structure of at least 5 carbon atoms, and/or with any of X or Y representing an oligomeric or a polymeric residue, which can optionally be substituted.

[0010] Preferably, X being R. More preferably, X and/or Y being an optionally substituted C₆-C₂₀ aryl group or an optionally substituted C₇-C₂₀ arylalkyl group; or X is an optionally substituted C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group. In another preferred embodiment, X is OH or an optionally substituted C-C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group. In still another preferred embodiment of the invention, X is an O-M⁺, with M⁺ representing an alkaline metal or earth alkaline metal cation, or an ammonium ion.

[0011] Examples of substituents are, for instance, groups such as halogens, amines groups, alcohols, ethers, polyalkyleneoxy residues, carboxylates, anhydrides, amides, ureas, urethanes, etc. Examples of polymeric residues are, for instance, polyethylene, polypropylene, polystyrene, polyethylene oxides, polypropylene oxides, polycarbonates, polyurethanes, polyesters, etc.

[0012] Preferably, from a processability point of view, the composition of the present invention contains a vicinal dioxoxygen containing component with a molecular weight of at least 200, preferably at least 500.

[0013] Examples of vicinal dioxoxygen containing components containing at least one 1,2 dioxo-moiety according to formula I that can suitably employed in the compositions according to the invention are, not limitative: 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 1-phenyl propanedione, pyruvic aldehyde, pyruvic acid, methylpyruvate, ethylpyruvate camphorquinone.

[0014] Examples of vicinal dioxoxygen containing components containing at least one 1,2 oxo-hydroxy moiety according to formula II that can suitably employed in the compositions according to the invention are, not limitative: acetal, dihydroxyacetone, dihydroxyacetone, benzoin, aryl substituted benzoins, furin, 2-hydroxypropanal, gluconic acid, methyl gluconate, gluconic acid, glyceric acid 3-hydroxybutanone.

[0015] Preferably, the amount of vicinal dioxoxygen containing component in the composition is at least 0.0001 wt. %, preferably at least 0.01 wt. % and even more preferably at least 0.1 wt. %, calculated on the total weight of the composition. Preferably, the amount of vicinal dioxoxygen containing component in the composition is lower than 10 wt. %. However, the amount of vicinal dioxoxygen containing component in the composition may vary within rather wide ranges, and may be chosen depending on the kind of application in which the composition of the invention is applied. The skilled man easily can assess, in dependence of the type of application selected, which amount thereof leads to good results.

[0016] The inventors have further found that the efficiency of oxygen-uptake is enhanced when the composition further contains an alkaline metal or earth alkaline metal salt or an ammonium salt. Preferably, the alkaline metal or earth alkaline metal salt is a K, Li or Na salt, preferably a K, Li or Na carboxylate. Generally, the carboxylates that can suitably be used in this preferred embodiment of the invention will be carboxylates having from 2 to 50 carbon atoms. Suitable carboxylates that can be used in this preferred embodiment of the present invention are, for instance, propionate, acetate, ethylhexanoate, lactate, butyrate. Also, for instance, stearates, palmitates, linoleates, linolenates, and oleates can suitably be used. Preferably the carboxylates used are carboxylates having at least 6 carbon atoms.

[0017] Preferably, the amount of the alkaline metal or earth alkaline metal salt or ammonium salt, if present, in the composition is at least 0.0001 wt. %, preferably at least 0.01 wt. % and even more preferably at least 0.1 wt. %, calculated on the total weight of the composition. Preferably, the amount of alkaline metal or earth alkaline metal salt or ammonium salt in the composition is lower than 10 wt. %.

[0018] In one embodiment of the invention, the oxidisable carbon containing component is a polymer. Suitable oxidisable polymers are organic polymers containing allylic positions; organic polymers containing tertiary carbons; organic polymers containing benzylic positions and organic polymers containing ether segments.

[0019] Examples of organic polymers containing allylic positions are butadiene containing (co)polymers; isoprene containing (co)polymers; cyclohexene copolymer, like for example ethylene-cyclohexene copolymers or polymers containing pendent 3-cyclohexenyl groups like ethylene-cyclohexenylmethyl acrylate copolymers and ethylene-methylac-

ylate-cyclohexenylmethyl acrylate terpolymers

[0020] Examples of organic polymers containing tertiary carbons are propylene containing (co)polymers, like for example propylene homopolymer or ethylene-propylene copolymer. Examples of organic polymers containing benzylic positions are m-xylylamine containing polyamides, like for example MXD6-polyamide. Preferred oxidisable polymers are organic polymers containing ether segments, for example polymers containing ethylene glycol, propylene glycol or tetramethylene glycol based segments. Preferred organic polymers containing ether segments are copolymers comprising propylene glycol segments, preferably 1,2-propylene glycol segments, and polymer segments. More preferably said copolymer comprising propylene glycol segments and polymer segments has been prepared by copolymerising the corresponding monomers in the presence of functionalised propylene glycol segments. To allow the monomers to attach on the propylene glycol segments these segments are functionalized with end groups that can react with reactive sites of the monomer. Examples of such functional end groups and reactive monomer sites are e.g. -OH-, -NH₂, acid, epoxy and other functional groups known in the art as reactive with polyamide monomers. Suitable propylene glycol segments are linear oligomers of propylene glycol and are of the substituted type. In IUPAC nomenclature this propylene glycol is denoted as polyoxy-1,2-propanediyl. They consist of 2 to 5000 propylene glycol monomer units, preferably of 10 to 2500 units and in this shape and size they have been copolymerised with the monomers. In this range an even distribution of the copolymers in the polycondensate appears to be achieved. During this copolymerisation copolymers of the -ABABA- type are formed comprising polymer segments A of variable length alternated with propylene glycol segments B.

[0021] In another embodiment the propylene glycol segments are present as branches in a two, three, four or higher star branched compound the centre unit of which can be e.g. a di-, tri-, tetra or higher functional ester, amide, ether, urethane. In the process of preparation of the copolymer applied in the composition of the invention, the polymer segments then grow from the free ends of the propylene glycol segment branches. During this copolymerisation linear copolymers can be formed of the type ABA or branched copolymers having branches of the type BA.

[0022] The polymer segments in the copolymers are preferably polyamide or polyester segments, more preferably polyamide segments. Examples of suitable polyesters are polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthanoate (PEN), polybutylene naphthanoate (PBN). Examples of suitable polyamides (PA) are aliphatic polyamides, that may eventually be branched polyamides, such as PA6, PA4,6, PA6,6, PA 11, PA12, semi aromatic polyamides as MXD6, PA6,1,6,T, PA6,6,6,T, fully aromatic polyamides and copolymers and blends of the listed polyamides and polyesters.

[0023] Suitable PPO segments are linear oligomers of PPO and are of the substituted type. In IUPAC nomenclature this PPO is denoted as polyoxy-1,2-propanediyl. They consist of 2 to 5000 polypropylene oxide monomer units, preferably of 10 to 2500 units and in this shape and size they have been copolymerised with the monomers. In this range an even distribution of the copolymers in the polycondensate appears to be achieved. During this copolymerisation copolymers of the -ABABA- type are formed comprising polymer segments A of variable length alternated with propylene oxide segments B.

[0024] In another embodiment the substituted PPO segments are present as branches in a two, three, four or higher star branched compound the centre unit of which can be e.g. a di-, tri-, tetra or higher functional ester, amide, ether, urethane. In the process of preparation of the copolymer applied in the composition of the invention, the polymer segments then grow from the free ends of the PPO segment branches. During this copolymerisation linear copolymers can be formed of the type ABA or branched copolymers having branches of the type BA.

[0025] Apart from the PPO segments also other ether segments optionally may be present as e.g. polyethylene oxide, however in smaller amounts than the PPO. Preferably the other ether segments are present in amounts less than 40 wt%, more preferably less than 30 wt% or less than 10 wt% of the amount of PPO. Also the PPO segments themselves may comprise a minority, i.e. present in amounts less than 40 wt%, more preferably less than 30 wt% or less than 10 wt% of the amount of PPO, of other poly(alkylene)oxide units, usually as co-blocks. An example of this is a block poly(ethylene)oxide-substituted PPO block-block poly(ethylene)oxide triblock segment.

[0026] In another embodiment of the invention, the oxidisable carbon containing component is an organic component containing allylic positions, like for example squalene, unsaturated fatty acids, castor oil, d-limonene or dihydroanthracene.

[0027] The composition according to the invention preferably further contains a polycondensate. The polycondensate is preferably (co)polyamide or (co)polyester or mixtures thereof, more preferably the polycondensate is polyamide.

[0028] Further the composition according to the invention may comprise other usual additives that may give a certain additional required property to the composition, examples of which are fibres, fillers, nano-particles, antioxidants, flame retardants, mould release agents and other compounds known in the art for this purpose.

[0029] In specifically preferred embodiments of the invention, the composition of the invention is essentially free of cobalt, most preferably free of cobalt. Essentially free of cobalt means that the cobalt concentration is lower than 10 ppm, preferably lower than 5 ppm and even more preferably lower than 1 ppm, calculated on the total weight of the composition. Even more preferably, the composition of the invention is essentially free of transition metal, most preferably

free of transition metal. Essentially free of transition metals means that the transition metal concentration is lower than 10 ppm, preferably lower than 5 ppm and even more preferably lower than 1 ppm, calculated on the total weight of the composition

[0030] The present invention further also relates to the use of the composition of the invention for the preparation of an oxygen-scavenging object, like for example a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap. In a preferred embodiment, the present invention relates to the use of the composition of the invention for the preparation of an object having at least one surface that is to be exposed to an oxygen containing environment, wherein the object comprises a layer containing the composition according to the invention. More in particular, the present invention relates to a multilayer object containing a layer of the composition of the invention. In one embodiment, the object is a multilayer object containing a layer of the composition of the invention wherein said layer being separated from a first surface of the object by one or more first layers having an overall oxygen permeability of at most 500 cm³/m². 24h.atm (when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 μm). In another embodiment, the composition is present in at least a layer forming a second surface of the object, opposite to the first surface, or being separated from said second surface by one or more second layers, the second layers having an overall oxygen permeability of more than 500 cm³/m². 24h.atm (when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 μm). In still another embodiment of the invention, the layer containing the composition is separated from a second surface of the object, opposite to the first surface, by one or more second layers, the second layers having an overall oxygen permeability of at most 500 cm³/m². 24h.atm (when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 μm).

[0031] The composition containing the oxidisable carbon-containing component and the vicinal dioxygen containing component can be prepared by mixing the oxidisable carbon-containing component with the vicinal dioxygen containing component in a separate step or in a step in the process of manufacturing the oxygen scavenging object. This mixing can be conducted in the equipment known in the art such as extruders and mixers. The process applies melt-mixing, i.e. the mixing takes place above the melting point of the oxidisable carbon-containing component but below its decomposition temperature.

[0032] The invention is now demonstrated by means of a series of examples and comparative examples. All examples are supportive of the scope of claims. The invention, however, is not restricted to the specific embodiments as shown in the examples.

Experimental part

Preparation of oxygen scavenging copolyetherester

[0033] A 2 l reactor equipped with distillation column and stirrer was charged with 410 g dimethylterephthalate, 290 g 1,4-butane diol, 550 g of a propyleneoxide based oligomer, 250 mg of titanium tetrabutoxide and 150 mg of magnesium acetate tetrahydrate.

[0034] After 3 times having flushed the reactor with nitrogen, the reactor content was heated under stirring and atmospheric pressure gradually within one hour to a temperature of 150°C, kept at this temperature for half an hour, and subsequently further heated within 2 hours to a temperature of 220°C. The thus obtained transesterified product was then further polymerised at 240°C under vacuum (down to 2 mbar) for 180 minutes at a stirring speed of 20 RPM. The polymerised product was released from the reactor, under nitrogen pressure, in the form of a strand, cooled in water, and granulated in a pelletizer.

Preparation of compounds

[0035] The copolyetherester granules were grinded. To these powder different vicinal dioxygen containing components were added as oxidation catalyst by solvent blending (adding the additives as a solution followed by evaporation of the solvent).

[0036] The effectivity of a catalyst was also determined in polypropyleneglycol (Mn 2700) (PPG) instead of the copolyetherester. In this case, the catalyst was mixed directly to the polypropylene glycol.

Examples I-VIII and Comparative Experiments A-B: Determination of the effectivity of the catalysts

[0037] The effectivity of the catalysts on the oxygen uptake rate of the copolymer was determined. In a vessel of 65 ml, to which a pressure transducer was connected, 1 gram polymer powder was brought into contact with an atmosphere containing 100% oxygen. The drop of the pressure in the vessel at 25 or 30 °C (depending on the polymer used) was recorded. From the drop in pressure, the oxygen uptake was calculated.

[0038] As a measure of the activity of the catalysts, the time to an oxygen uptake of 50 mmol/kg was determined. The

results are shown in Table 1 and Table 2.

Table 1: Effectivity of catalysts in the copolyether ester at 25°C

Example	Catalyst	Amount catalyst (wt%)	Cocatalyst	Amount cocatalyst (mmol/kg)	Time to an oxygen uptake of 50 mmol/kg (minutes)
I	Phenylpropanedione	0.5	-		230
II	Phenylpropanedione	1			130
III	Phenylpropanedione	0.1	Potassium octanoate	1.5	420
IV	Phenylpropanedione	0.25	Potassium octanoate	1.5	130
V	Phenylpropanedione	0.5	Potassium octanoate	0.5	100
VI	Phenylpropanedione	0.5	Potassium octanoate	1.5	45
VII	Butanedion	1	-		1300
VIII	Camperdion	1	Potassium octanoate	1.5	14000
VIII	Benzoine	1			7150
VIII	Benzoine	1	Potassium octanoate	1.5	6900
A	-	-	-	-	>20.000
B	Cobalt-acetate	0.1			1000

Table 2: Effectivity of catalysts in PPG at 30°C

Example	Catalyst	Amount catalyst (wt%)	Cocatalyst	Amount cocatalyst (mmol/kg)	Time to an oxygen uptake of 50 mmol/kg (minutes)
I	Butanedion	1.0	-		5000
C	Cobalt-acetate	0.1			>7000

[0039] The examples and comparative experiments clearly demonstrate the oxygen scavenging capacity of compositions according to the invention. Furthermore they clearly demonstrate the enhanced efficiency which can be obtained by adding a cocatalyst according to the invention. Furthermore they demonstrate that multiple polymers can be used according to the invention. In addition, it is shown that the use of certain vicinal dioxygen containing components even results in that the oxygen scavenging properties of the composition are more efficient, i.e. the rate of oxygen-uptake is higher, compared to the use of a cobalt compound as oxidation catalyst.

Claims

- Composition containing an oxidisable carbon-containing component, **characterized in that** the composition further contains a vicinal dioxygen containing component.
- Composition according to claim 1, **characterized in that** the vicinal dioxygen containing component contains at

least one 1,2-dioxo-moiety according to formula



with X and Y being identical or different from each other, and representing respectively:

X, Y: OR, SR, NR₁R₂, R, O-M⁺;

R, R₁, R₂: a group selected from the groups consisting of H, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₆-C₂₀ aryl group, an optionally substituted C₇-C₂₀ alkylaryl group, and an optionally substituted C₇-C₂₀ arylalkyl group,

M⁺ being a cation

and wherein X and Y may be joint together to form a vicinal dioxo cyclic structure of at least 5 carbon atoms, and/or with any of X or Y representing an oligomeric or polymeric residue.

3. Composition according to claim 2, **characterised in that** X and/or Y being R.

4. Composition according to claim 2, **characterised in that** X and Y being R.

5. Composition according to claim 2, **characterised in that** X or Y being an optionally substituted C₆-C₂₀ aryl group or an optionally substituted C₇-C₂₀ arylalkyl group.

6. Composition according to claim 2, **characterised in that** X is an optionally substituted C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group.

7. Composition according to claim 2, **characterised in that** X is OH or an optionally substituted O-C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group.

8. Composition according to claim 2, **characterised in that** X and/or Y is an O-M⁺, with M⁺ representing an alkaline metal or earth alkaline metal cation, or an ammonium ion.

9. Composition according to claim 1, **characterized in that** the vicinal dioxoxygen containing component contains at least one 1,2-oxo-hydroxy moiety according to formula II



with X and Y being identical or different from each other, and representing respectively:

X: OR, SR, NR₁R₂, R, O-M⁺; Y: OR, SR, NR₁R₂, R;

R, R₁, R₂: a group selected from the groups consisting of H, an optionally substituted C₁-C₂₀ alkyl group, an optionally substituted C₆-C₂₀ aryl group, an optionally substituted C₇-C₂₀ alkylaryl group, and an optionally substituted C₇-C₂₀ arylalkyl group,

M⁺ being a cation

and wherein X and Y may be joint together to form a vicinal dioxo cyclic structure of at least 5 carbon atoms, and/or with any of X or Y representing an oligomeric or a polymeric residue.

10. Composition according to claim 9, **characterised in that** X being R.

11. Composition according to claim 9, **characterised in that** X and/or Y being an optionally substituted C₆-C₂₀ aryl group or an optionally substituted C₇-C₂₀ arylalkyl group.

12. Composition according to claim 9, **characterised in that** X is an optionally substituted C₁-C₂₀ alkyl group and Y is an optionally substituted C₆-C₂₀ aryl group.
- 5 13. Composition according to claim 9, **characterised in that** X is OH or an optionally substituted OC₁-C₂₀ alkyl group and Y an optionally substituted C₆-C₂₀ aryl group
14. Composition according to claim 9, **characterised in that** X is an O⁻ M⁺, with M⁺ representing an alkaline metal or earth alkaline metal cation, or an ammonium ion.
- 10 15. Composition according to any one of claims 1-14, **characterised in that** the composition further contains a K, Li or Na salt.
16. Composition according to any one of claims 1-15, **characterised in that** the oxidisable carbon containing component is an organic polymer containing allylic positions, preferably a butadiene containing (co)polymer, an isoprene containing (co)polymer, a cyclohexene copolymer or a polymer containing pendant cyclohexenyl groups.
- 15 17. Composition according to any one of claims 1-15, **characterised in that** the oxidisable carbon containing component is an organic polymer containing tertiary carbons, preferably a propylene containing (co) polymer.
- 20 18. Composition according to any one of claims 1-15, **characterised in that** the oxidisable carbon containing component is an organic polymer containing benzylic positions, preferably a m-xylylamine containing polyamide.
19. Composition according to any one of claims 1-15, **characterised in that** the oxidisable carbon containing component is an organic polymer containing ether segments.
- 25 20. Composition according to claim 19, **characterised in that** the ether segments are ethylene glycol, propylene glycol or tetramethylene based segments.
- 30 21. Composition according to claim 20, **characterised in that** the organic polymer containing ether segments is a copolymer comprising 1,2-propylene glycol based segments and polymer segments.
22. Composition according to claim 21, **characterised in that** the copolymer comprising 1,2-propylene glycol based segments and polymer segments has been prepared by copolymerising the corresponding monomers in the presence of functionalised 1,2-propylene glycol segments.
- 35 23. Composition according to claim 21 or 22, **characterised in that** the polymer segments are polyamide or polyester.
24. Composition according to any one of claims 1-15, **characterised in that** the oxidisable carbon containing component is an organic component containing allylic positions.
- 40 25. Composition according to claim 24, **characterised in that** the organic component containing allylic positions is squalene, an unsaturated fatty acid, castor oil, d-limonene or dihydroanthracene.
26. Composition according to any one of claims 1-25, **characterised in that** the composition further contains a polycondensate.
- 45 27. Composition according to claim 26, **characterised in that** the polycondensate is (co)polyamide or (co)polyester or mixtures thereof.
- 50 28. Composition according to any one of claims 1-27, **characterised in that** the composition is essentially free of cobalt.
29. Use of the composition according to any one of claims 1-28 for the preparation of an oxygen-scavenging object.
30. Use according to claim 29, wherein the object is a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap.
- 55 31. Use according to claim 29, wherein the object is a multilayer object containing a layer of the composition and wherein said layer being separated from a first surface of the object by one or more first layers having an overall oxygen

permeability of at most $500 \text{ cm}^3/\text{m}^2 \cdot 24\text{h} \cdot \text{atm}$.

32. Use according to claim 29, wherein the composition is present in at least a layer forming a second surface of the object, opposite to the first surface, or being separated from said second surface by one or more second layers, the second layers having an overall oxygen permeability of more than $500 \text{ cm}^3/\text{m}^2 \cdot 24\text{h} \cdot \text{atm}$.

33. Use according to claim 29, wherein the layer containing the composition is separated from a second surface of the object, opposite to the first surface, by one or more second layers, the second layers having an overall oxygen permeability of at most $500 \text{ cm}^3/\text{m}^2 \cdot 24\text{h} \cdot \text{atm}$.

34. Object, having at least one surface that is to be exposed to an oxygen containing environment, characterised in that the object comprises a layer containing the composition according to anyone of claims 1-28.

35. Object according to claim 34, wherein the object is a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap.



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 06 01 4331 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2004/129554 A1 (SOLIS JAMES A [US] ET AL) 8 July 2004 (2004-07-08) * paragraphs [0098], [0117] * * paragraphs [0057], [0076] * * paragraphs [0082] - [0092] * * example 1 *	1, 9-13, 28-35	INV. C09K15/08
X	US 2004/086749 A1 (KENNEDY THOMAS D [US] ET AL) 6 May 2004 (2004-05-06) * paragraphs [0154] - [0161] * * claims 1,2,4 *	1-7, 9-13, 16, 23, 28-30, 34, 35	
X	WO 98/12250 A (GRACE W R & CO [US]; MIRANDA NATHANIEL R [US]; SPEER DREW V [US]) 26 March 1998 (1998-03-26) * claims 1-5 *	1, 9-13, 16, 23, 28-30, 34, 35	
	----- -/-		TECHNICAL FIELDS SEARCHED (IPC) C09K C08K
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/does not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely:</p> <p>Claims searched incompletely:</p> <p>Claims not searched:</p> <p>Reason for the limitation of the search: see sheet C</p>			
Place of search Munich		Date of completion of the search 31 October 2006	Examiner Russell, Graham
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p>			

3
EPC FORM 1503 (05.05.04) (P4007)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 06 01 4331

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	EP 1 032 038 A2 (NAT STARCH CHEM INVEST [US]) 30 August 2000 (2000-08-30) * claims 1-3 *	1, 9-13, 28-30, 34, 35	
E	EP 1 705 216 A (DSM IP ASSETS BV [NL]) 27 September 2006 (2006-09-27) * examples *	1-7, 23, 24, 28	
E	WO 2006/083381 A (UNIV MARYLAND [US]; VARMA SHAMBHU D [US]; PETRALI JOHN [US]) 10 August 2006 (2006-08-10) * paragraph [0019] *	1-14	
A	US 5 958 254 A (ROONEY MICHAEL LAURENCE [AU]) 28 September 1999 (1999-09-28) * example 6 * * claims *	1, 2, 9, 29, 34	TECHNICAL FIELDS SEARCHED (IPC)
A	US 4 886 618 A (NOVAK RONALD W [US] ET AL) 12 December 1989 (1989-12-12) * claims *	1, 2, 9, 29, 34	



European Patent
Office

INCOMPLETE SEARCH
SHEET C

Application Number

EP 06 01 4331

Claim(s) searched incompletely:
1,15-19,24-26,28,29,34

Claim(s) not searched:
-

Reason for the limitation of the search:

The present claim 1 relates to an extremely large number of possible compositions. Ther terms "oxidisable carbon-containing component" and "vicinal dioxygen containing component" are not further defined in claim 1 and are extremely broad. The former term comprises a huge amount of possible organic compounds and polymers; while the latter term also relates to a vast majority of components both inorganic, organic, and polymeric. The term "vicinal" itself may mean by definition neighbouring oxygens, oxygens lying in consecutive order, and/or oxygens being adjacent to each other, and is in no way limited to the structures given in the formulae I and II of current claims 2 and 9. Support and disclosure in the sense of Article 84 and 83 EPC is to be found however for only a very small proportion of the compounds claimed, see the formulae I and II, page 3 of the description, and the Examples [Table 1].

As the technical features of claim 1 are not clearly defined, this would require an equally unquantifiable and thus unreasonable amount of experimentation from the skilled person, and thus imposes a severe and undue burden on all those wishing to ascertain the scope of the claim, which is not in compliance with the clarity requirement of Article 84 EPC.

In addition, the initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of these claims may be said to define subject-matter for which protection might legitimately be sought (Article 84 EPC).

The non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 45 EPC and Guidelines B-VIII, 3). The extent of the search was consequently limited.

The search of claims 1, 15-19, 24-26, 28, and 29 was restricted to the components which appear to be supported. The claimed "oxidisable carbon-containing components" were restricted to those components described in the description 4-6 and in claims 16-25; and the "vicinal dioxygen containing component" to those compounds of the formula I and II [for the understanding of "vicinal"] and described on page3 and Table 1 of the description.

As a result the subject-matter of claims 1, 15-19, 24-26, 28, and 29 could only be incompletely searched.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 01 4331

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-10-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004129554 A1	08-07-2004	NONE	
US 2004086749 A1	06-05-2004	CA 2449786 A1 EP 1393064 A1 JP 2004535571 T MX PA03011228 A NZ 529825 A WO 02099416 A1 US 2003082321 A1	12-12-2002 03-03-2004 25-11-2004 26-02-2004 19-12-2003 12-12-2002 01-05-2003
WO 9812250 A	26-03-1998	AT 197715 T AU 733336 B2 AU 4422097 A CA 2265755 A1 DE 69703587 D1 DE 69703587 T2 DK 927221 T3 EP 0927221 A1 ES 2153215 T3 JP 2000503339 T JP 3212097 B2 NZ 334655 A	15-12-2000 10-05-2001 14-04-1998 26-03-1998 28-12-2000 31-05-2001 11-12-2000 07-07-1999 16-02-2001 21-03-2000 25-09-2001 29-09-2000
EP 1032038 A2	30-08-2000	CN 1267891 A JP 2000273317 A KR 2000058019 A US 6344157 B1	27-09-2000 03-10-2000 25-09-2000 05-02-2002
EP 1705216 A	27-09-2006	WO 2006100123 A1	28-09-2006
WO 2006083381 A	10-08-2006	NONE	
US 5958254 A	28-09-1999	AT 266710 T WO 9412590 A1 CA 2149542 A1 CN 1096315 A DE 69333514 D1 DE 69333514 T2 DK 670871 T3 EP 0670871 A1 ES 2220910 T3 JP 2922306 B2 JP 8504851 T MX 9307372 A1 NZ 258043 A US 6346200 B1	15-05-2004 09-06-1994 09-06-1994 14-12-1994 17-06-2004 12-05-2005 20-09-2004 13-09-1995 16-12-2004 19-07-1999 28-05-1996 29-07-1994 26-07-1996 12-02-2002

EPO E-PUB PAGE

For more details about this annex : see Official Journal of the European Patent Office, No 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 01 4331

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-10-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4886618	A	12-12-1989	NONE

EPO Form P468

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82